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THE MANUFACTURING METHOD OF SURFACE DECARBONIZED STEEL SLAB WITH EXCELLENT SULFIDE STRESS CORROSION AND AMMONIA CRACKING RESISTANCE

Translation of Japanese Patent, JP #57-149421, Japan Kokai Tokkyo Koho

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16. Abstract

This manufacturing method of surface decarbonizing steel with excellent sulfide stress corrosion and ammonia cracking resistance is described with distinctive characteristics.

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DETAILS /103

1. NAME OF INVENTION:

The manufacturing method of surface decarbonized steel with excellent sulfide stress corrosion and ammonia cracking resistances.

2. SCOPE OF PATENT REQUEST:

This manufacturing method of surface decarbonized steel with excellent sulfide stress corrosion and ammonia cracking resistance has the following distinctive characteristics:

When the slab is heated in a furnace before it goes through pressure expansion under heating, oxygen concentration in the atmosphere shcuild be 0.1% through 3%, the dew point should be controlled at equal to or below 25°C, and the duration in the furnace should be equal to or more than the time given by the following equation:

$$t = 0.19\ (x + 2.2)^2 \text{ hours,}$$

where x is the pressure rate during pressure expansion under heating.

3. DETAILED EXPLANATION OF INVENTION:

This invention deals with the manufacturing method of surface decarbonized steel with excellent sulfide stress corrosion and ammonia cracking resistances, and in detail deals with the method of the surface decarbonization treatment during slab heating before the pressure expansion under heating.

As the raw steel for LPG, the development of steel is under way which has the qualities of excellent sulfide stress corrosion cracking resistance and of 60 * steel. To improve the characteristics of the sulfide stress corrosion cracking resistance, it is necessary to hold the hardness of the melted part equal to or below H [v] 250 (ref. Tanimura, Japan Steel Organization Seminar Conference (1977) P.S381). Therefore, treatments such as cladding are proposed. But the cladding increases the manufacturing cost extremely, and material quality is another problem.

This invention intends to solve the problem mentioned above. It proposes the manufacturing method of surface softened steel while lowering the hardness of the area affected by heat at equal to or under H [v] 250 by surface decarbonization treatment. Yet the cost is low, and there are no material quality problems.

Therefore, this invention deals with the following distinctive feature in slab heating: When the slab is heated in a furnace before it goes through pressure expansion under heating, the oxygen concentration in the atmosphere should be controlled at 0.1%-3%, the dew point should be controlled at equal to or below 25°C, and the duration in the furnace should be equal to or more than the time given by the following equation:

$$t = 0.19\ (x + 2.2)^2 \text{ hours},$$

where x is the pressure rate during pressure expansion under heating.

The following is the detailed explanation of the method of this invention.

First, this invention deals with the method to cost effectively decarbonize the surface of raw steel in order to improve the characteristics of sulfide stress corrosion and ammonia cracking resistances.

In recent years, studies have been made to take measures for surface softening to develop steel with excellent characteristics of sulfide stress corrosion cracking resistance. Among these studies are soft steel cladding and other techniques, and among these techniques is the surface decarbonizing method. To perform surface decarbonization, the atmosphere should be set within the oxidizing region for carbon (C in the following discussion) and without a very active oxidizing region for iron (Fe in the following discussion). The raw steel needs to be heated at equal to or above the AC_1 point for a long time. The higher the temperature, the better the results. Considering the present quality of

manufacturing processes, the repeated decarbonizing method during slab heating can be taken into account. As a result of the studies of this method, the sulfide stress corrosion cracking resistance is improved extremely during an ordinary slab heating process (temperature 1100°C-1300°C) prior to the pressure expansion process under heating, under the following conditions: The oxygen concentration in the atmosphere is controlled within 0.1% through 3%, the dew point is controlled at equal to or below 25°C, and the duration in the furnace is equal to or more than the time given by the equation:

$$t = 0.19\ (x + 2.2)^2 \text{ hours,}$$

where x is the pressure ratio.

The details are explained below. First, in order to decarbonize the raw steel most effectively, the necessary chemical condition is * to accelerate the decarbonization by carbon within the steel. In order to do this, the chemical reaction must progress in such a way that the value of C becomes zero or close to zero. On the other hand, decarbonization is a phenomenon in which C is oxidized. In the atmosphere of decarbonizing C, Fe is also oxidized, so that it is possible to decrease the apparent decarbonization. Therefore, in order to decarbonize effectively, the heating should be done in an atmosphere which suppresses the oxidation of Fe as much as possible and at the same time accelerates the oxidation of C. Therefore, in order to employ decarbonization treatment in the present slab heating process, 0_2 and H_20 must be controlled in the slab heating atmosphere. According to the studies of the inventors of this paper, in order to decarbonize effectively at a high temperature between 1100°C-1300°C, such as the case in the slab heating, it was found that the amount of 0_2 in atmospheric gas should be controlled between 0.1% through 3%, and the dew point should be equal to or below 25°C. In an ordinary steel plate manufacturing process, pressure expansion under heating is performed after heating the slab, but the decarbonized film is decreased during heating of the slab by the pressure (x to be set as the pressure ratio of this case).

Therefore, in order to obtain a decarbonized film which effectively enhances the characteristics of sulfide stress corrosion cracking resistance in the steel plate, the slab heating duration (with the consideration of decreasing decarbonized film under pressure) must be equal to or more than the time given by the equation:

$$t = 0.19\ (x + 2.2)^2 \text{ hours.}$$

In this case, the pressure ratio should be set preferably between 3 to 6 and the duration in the furnace should be set to 5.1 to 12.8 hours in order to obtain good material economically.

The following explains these conditions:

First, take the oxygen concentration in the atmospheric gas which is in the proper range of equal to or more than 0.1%-3%. This range is determined because if the oxygen concentration becomes 0.1% or below, the decarbonization effect decreases and therefore it becomes economically infeasible. If it becomes 3% or more, the decarbonized film decreases due to oxidation of Fe. And the * point should be set at equal to or below 25°C. If it is equal to or above 25°C, the decarbonized film decreases due to oxidation of Fe. Next, the slab heating duration, which is determined by the pressure ratio in pressure expansion, should be equal to or more than the number of hours given by the equation:

$$t = 0.19\ (x + 2.2)^2.$$

If it is less than this duration, it becomes impossible to retain a width of the decarbonized film in the steel plate sufficient enough to improve the characteristics of sulfide stress corrosion crack resistance, because the decarbonized film decreases during the pressure expansion. And it is desirable to set the pressure ratio x between 3 to 6, and the duration in the furnace t to be 5.1 hours to 12.8 hours, because if the pressure rate x is set equal to or less than 3, then cracks remain in the steel plate. If the pressure ratio x is set equal to or more than 6, then the slab heating duration is increased accordingly and becomes more than 12.8 hours. This increases the cost and the economical

advantage of surface decarbonized steel is lost.

Next, the * is explained.

First, the slab of 60 kg/mm^2 steel with chemical composition of the steel shown in Table 1 is heated under the heating conditions shown in Table 2. In this, conditions 1 through 7 are for this invention method and conditions 8 through 14 are listed for comparison purposes. Next, when the slab is heated under conditions in Table 2, pressure expansion is performed using the ordinary method, then quenched at 930°C for 60 minutes, and then tempered at 680°C for 70 minutes. With this treatment, the steel plate was made. Using this steel plate, the following test was done to see if there were cracks in the material: From the test material surface which is welded with heating of 12,000 J/cm, a piece is collected for the stress corrosion crack test using constant distortion bending with four point support. The stress using the four point bending is changed to 50 to 30 kg/mm^2 and then it is checked for cracks after being soaked under the corrosive atmosphere of 0.5% CH_3, COOH + 3000 ppm H_0S for a period of 500 hours. The result is shown in Table 3, and the table shows that the steel made by this invention method alone had the excellent characteristics of sulfide stress corrosion crack resistance. The relationship between the oxygen content in the heated atmosphere and the decarbonized carbon content (shown in the carbon content 3 mm below the surface) during slab heating is shown in Figure 1. The relationship between the dew point and the decarbonized carbon content (shown in the carbon content 3 mm below the surface) is shown in Figure 2. These figures show that the decarbonized carbon content decreases rapidly as the oxygen content rises above 3%, and as the dew point rises at equal to or above 25°C.

TABLE 1. Chemical composition (wt %)

C	Si	Mn	P	S	Cu	Ni	Cr	Mo	V	Al
013	0.32	1.30	0.023	0.003	0.02	0.08	0.02	0.070	0.042	0.040

TABLE 2. Slab heat condition and pressure rate

	③鋼種	④加熱温度(℃)	⑤時間(hr)	⑥露点(℃)	⑦O_2濃度(%)	⑧圧下比
①	1	1200	5.2	10	0.5	3
	2	〃	5.2	10	2.5	3
	3	〃	10.0	10	0.5	5
	4	〃	10.0	10	2.5	5
	5	〃	10.0	20	2.5	5
	6	〃	13.0	10	0.5	6
	7	〃	13.0	10	2.5	6
②	8	〃	3.0	10	2.5	3
	9	〃	8.0	10	2.5	5
	10	〃	10.0	10	2.5	6
	11	〃	10.0	10	4.0	5
	12	〃	10.0	10	6.0	5
	13	〃	10.0	30	2.5	5
	14	〃	10.0	60	2.5	5

1--this invention condition; 2--comparative condition; 3--steel no.; 4--temperature (°C); 5--period (or time) hr; 6--dew point (°C); 7--0_2 concentration (%); 8--pressure rate

TABLE 3. Result of stress corrosion crack test *

	③鋼種	④曲げ応力(kg/mm²) 50	45	40	35	30
①	1	○	○	○	○	○
	2	○	○	○	○	○
	3	○	○	○	○	○
	4	○	○	○	○	○
	5	○	○	○	○	○
	6	○	○	○	○	○
	7	○	○	○	○	○
②	8	×	×	○	○	○
	9	×	×	×	○	○
	10	×	×	○	○	○
	11	×	×	×	×	○
	12	×	×	×	×	○
	13	×	×	×	○	○
	14	×	×	×	×	○

○ 割れなし ⑤
× 割れあり ⑥

1--this invention condition; 2--comparative condition; 3--steel no.; 4--bending stress kg/mm²; 5--(circle) no crack; 6--x crack found

To summarize, this invention deals with a method to control the atmosphere during slab heating and the heating duration, but if this method is employed with the surface softening treatment, the characteristics of ammonia crack resistance can be improved.

The surface softening treatment in this case means that the cooling rate of the steel surface should be decreased during the quenching cooling process, or that the quenching is made difficult by keeping the sample below the Ar point.

4. BRIEF EXPLANATION OF FIGURES:

Figure 1 shows the relationship between the oxygen content and the decarbonized carbon content. The test condition is at 1200°C for 10 hours with the dew point at 10°C. Figure 2 shows the relationship between the dew point and the decarbonized carbon content. The test condition is at 1200°C for 10 hours with the oxygen content 2.5%.

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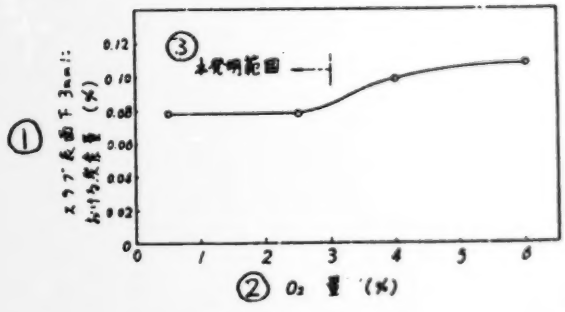

Figure 1
1--content of carbon 3mm below the slab surface (%);
2--content of oxygen (%);
3--range of this invention

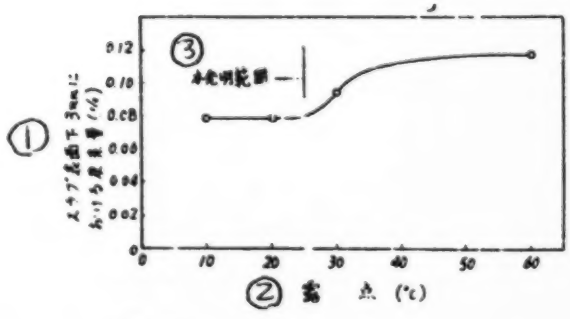

Figure 2
1--content of carbon 3 mm below the slab surface (%);
2--dew point (°C);
3--range of this invention